

Sampling and Analysis Plan
for the
2009/2010 Heavy Metals Concentration of Stream Sediment
and Floodplain Soil Within the 6TREATY Tribes
Historic Jurisdictional Lands
Ottawa and Delaware Counties, Oklahoma

November 4, 2009

Prepared by:

6TREATY Tribes of Oklahoma

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1.0 Introduction

1.1 Sampling and Analysis Plan for the 2009/2010 Heavy Metals Assessment Study Within the 6TREATY Tribes Historic Jurisdictional Lands

A sampling and analysis plan (SAP) integrates the three primary elements into one plan including, a Quality Assurance Project Plan (QAPP), a Field Sampling Plan (FSP), and Health and Safety Plan (HSP). The QAPP describes the policy, organization, functional activities, quality assurance and quality control protocols necessary to achieve project data quality objectives (DQOs) dictated by the intended use of the data. The FSP provides guidance for all fieldwork by detailing the sampling and data gathering methods to be used on the project. This document includes the essential elements of both a QAPP and FSP. This document describes the sampling and analysis that will be conducted in December 2009/January 2010 to assess soil quality conditions within the 6TREATY historical jurisdictional areas. More specifically, this document includes the following components:

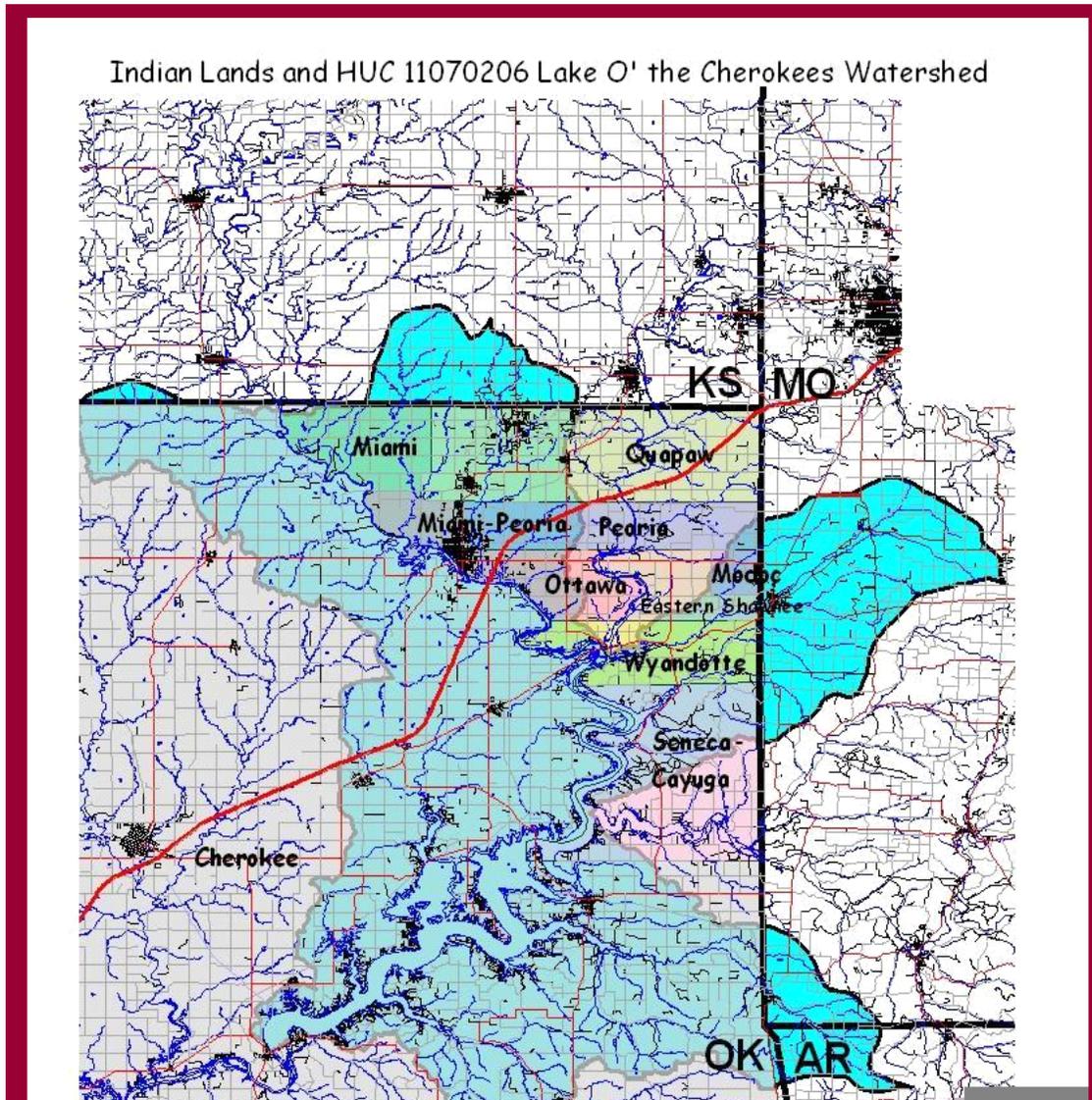
- Introduction (Section 1);
- Sampling objectives (Section 2);
- Sampling program design (Section 3);
- Sampling locations and frequency (Section 4);
- Sampling timing (Section 5);
- Sample designation (Section 6);
- Sampling equipment and procedures (Section 7);
- Sample handling and analysis (Section 8)
- Contaminants of potential concern (Section 9);
- Roles and responsibilities of the sampling team (Section 10);
- Quality assurance (Section 11);
- Examples of forms and instructions for completing paperwork (Section 12);
- References (Section 13).

2.0 Sampling Objectives

The 2009/2010 Heavy Metals Assessment Study Within the 6TREATY Tribes Historic Jurisdictional Lands is intended to provide the information needed to determine the extent of soil degradation from historic mining operations in the 6TREATY historical jurisdictional areas (Figure 1). More specifically, the objectives of the SAP are to:

1. Obtain data on target metal concentrations for approximately 72 soil samples collected from Delaware and Ottawa County, Oklahoma in potential depositional areas resulting from historic mining operations. The samples collected will be dried and an X-ray fluorescence (XRF) analysis performed in accordance with EPA Method 6200.
2. Confirm results of XRF-based metal analyses by submitting a minimum of 5% of the collected samples for laboratory analysis. Samples will be sieved to <63 microns, digested following EPA Method 3052, and analyzed by Inductively Coupled Plasma/Atomic Emission Spectrometry (ICP-AES, EPA Method 6010B).

Tribal Historical Jurisdiction Map



3.0 Sampling Program Design

Soil sampling will take place in December 2009 and January 2010 over the course of two to three weeks. Two sampling teams comprised of two to three people will collect approximately 72 samples. Each sample will be analyzed using XRF technology, as indicated in Section 7.0. A minimum of 5% of the samples will be corroborated through laboratory analysis.

4.0 Sampling Locations and Frequency

The sampling locations (i.e., riverine) for the 2009/2010 Heavy Metals Assessment Study Within the 6TREATY Tribes Historic Jurisdictional Lands will be selected based on the following parameters:

- GPS Coordinates
- Tribal jurisdictional boundaries
- Within 100 year flood plain

Sampling locations will be identified based on the parameters outlined above. Landowner/Tribal permission will be obtained for property access. Samples will be collected at the identified locations unless unsafe conditions exist or landowner permission is not received. In these situations, alternative sampling locations will be identified. If an acceptable alternative location cannot be identified, then no sample will be collected. GPS coordinates will be taken for all sampling points/transects.

5.0 Sampling Timing

The soil samples for the 2009/2010 Heavy Metals Assessment Study Within the 6TREATY Tribes Historic Jurisdictional Lands will be collected in December of 2009 and January of 2010 if necessary. Approximately 72 soil samples will be collected. Soil metal concentrations from historic mining are stable relative to time frames measured in months. Soil/sediment sampling within this short timeframe should not have a significant effect on results.

6.0 Sample Designation and Procedures

6.1 Sample Collection Procedures

A map of historic jurisdictional areas will be used to indicate where to begin each transect. Sampling locations (i.e. historic jurisdictional areas) will be identified using the parameters outlined in Section 4.0. Transects will be from the middle of the river and up to the 100 year historic flood plain if possible.

Each transect will start at the middle of the river to the respective historic floodplain boundaries. Samples will be collected along each transect, approximately 4 to 5 samples will be obtained (at least 1 sediment from river and 3 soil from floodplain). The number of samples per transect may change depending upon the width of the water body and the floodplain within a designated transect. It is anticipated that there will be at least 1 transect per $\frac{1}{4}$ mile of water body that is within the historical jurisdictional areas.

At each sampling collection point, all plant material and organic detritus will be removed from the surface; the sampler (e.g. sharp shooter, shovel, and trowel) will be used to gather the sample from a depth of 1-6 inches.

The soil sample will be placed into a 1 liter zip lock bag and labeled appropriately. Split samples will be used for quality assurance and confirmatory laboratory analysis, requiring two bags (a minimum of 5% of all samples will be sent to the laboratory for confirmatory analysis). All samples will be dried and sieved to <63 microns. The split sample will be sent to a qualified lab for analysis by EPA Method 3052 to confirm the results of the field chemistry results. The remaining samples will be analyzed with the XRF using EPA Method 6200 by certified tribal personnel.

Before a new transect is sampled, the sampling equipment will be cleaned by removing any excess soil and inserting into the soil near the sample location. Between each transect, the sampler will be rinsed with deionized water, followed by Liquinox, and deionized water, then placed in a stainless steel tray for transport between transects. Alternatively, a pre-cleaned dedicated sampling spoon or scoop will be used at each sampling location.

Table 1 lists the equipment that will be used to collect samples for the 2009/2010 Heavy Metals Assessment Study Within the 6TREATY Tribes Historic Jurisdictional Lands (see Appendix A). The following information will be recorded following retrieval of the sample:

- Unusual events that occurred during sampling;
- Sample depth;
- Description of sample (i.e. sandy, clay etc);
- Description of sample color (i.e., black, brown, etc.); and
- Sample processing procedure used (i.e., total volume collected, type of containers used).

6.2 Precautions to Avoid Exposure to Contaminated Soil

It is anticipated that contaminated soil will be routinely encountered during sampling throughout much of the study area. As such, the sampling crew should take precautions to minimize exposure to potentially toxic substances. At a minimum, steps that should be taken include:

- Handling sampling equipment and samples carefully;
- Avoiding direct dermal contact with samples; and,
- Wearing protective equipment, such as gloves, safety glasses, long-sleeved shirts, long pants, rubber boots, and/or rain gear.

More detailed guidance on avoiding hazards during sampling and minimizing the potential for personal injury is provided in the Health and Safety Plan (Appendix A)

6.3 Other Precautions to Avoid Sample Contamination

Generation of reliable data for soil quality conditions is the primary objective of this sampling event. As such, all reasonable efforts should be made to minimize the potential for sample contamination during the sample collection, handling, and processing. At a minimum, steps that should be taken to avoid sample contamination include:

- Ensuring that samples do not come in contact with any item that has not undergone the approved decontamination process;
- Ensuring that any utensils that are used in the sampling process do not come in contact with any item that has not undergone the approved decontamination process;
- Decontaminating all sampling equipment fully after sampling is completed; and,
- Prohibiting any activity that could result in sample contamination (e.g., smoking, consumption of food or drinks during the sampling event). Note: A separate cooler for food and drinks will be available.

6.4 Information to be Collected at Sampling Locations

The following basic information will be collected and recorded at each sampling location on the data collection form:

- Sample location name and number;
- Sampling date and time;
- Latitude and longitude coordinates in WGS84 datum using decimal degrees;
- Weather conditions, including precipitation, temperature etc.;
- Type of sampler used;
- Names of sampling personnel;
- Soil type/soil genesis; and
- In-situ XRF results for Pb, Zn, and Cd.

7.0 Sample Handling and Preparation

Procedures for handling and preparing samples for metal analysis should follow the procedures described in ASTM (2004; also Appendix A -Table 2). Samples should be carefully packed and transferred to the appropriate laboratory for storage along with the appropriate chain of custody forms. If samples are shipped, an inventory must be maintained of all samples that are shipped each day to facilitate confirmation of receipt the following business day. All samples will be dried and sieved to <63microns. The samples selected for confirmatory chemical analysis (i.e. split samples) will digested using EPA Method 3052 (Microwave assisted acid digestion of siliceous and organically based matrices) and analyzed by ICP-AES using EPA Method 6010B.

The remaining samples will be analyzed with the XRF using EPA Method 6200.

8.0 Chemicals of Potential Concern

Previous studies in the Tri-State Mining District have identified cadmium, lead, and zinc as the primary contaminants elevated due to mining activity (Dames & Moore, 1995). The adverse biological effects of these metals are well documented (Eisler 2004). In order to identify potential injury from mining activity, samples will be analyzed for these target metals. The list of priority analytes and associated data quality objectives for the chemical analyses are presented in Appendix B - Table 3.

9.0 Roles and Responsibilities of Sampling Team

Samples supporting the Heavy Metals Assessment Study Within the 6TREATY Tribes Historic Jurisdictional Lands will be systematically collected within the sampling area. The sampling teams will be comprised of two to three individuals with responsibility for collecting and preparing samples, conducting on-site XRF analyses of samples, and preparing and shipping samples for lab analysis. Quality assurance and control (QA/QC) for the field portion of this investigation will be directed by Meredith Garvin, Tribal Environmental Management Services (TEMS).

The sample collection teams will:

- ensure that all necessary sampling equipment and supplies are loaded into the sampling vehicle(s) each day,
- verify the sample locations (using handheld GPS),
- collect sufficient soil volumes for analyses of soil chemistry,
- prepare and label samples,
- decontaminate the samplers between transects, and
- follow the completion of sampling activities at each location.

One team member will perform the XRF analysis; a second team member will collect the soil samples and decontaminate the sampler; and the third team member will collect the GPS readings and take field notes.

Samples will be transported in a secure manner to avoid damage to the sample. Any samples lost or damaged during transport must be identified by sampling location and documented. If a commercial shipping service is used, soil samples may be shipped on Monday, Tuesday, Wednesday, Thursday, and Sunday only (to avoid weekend delivery issues). Any soil samples not shipped on the date of collection will be held and shipped on the next appropriate shipping day. Unused portions of samples will be disposed of at the sampling location where collected.

Sample collection and disposition will be clearly documented. At each sampling location, the data collection form will be filled out (see example in Addendum A). Samples will be stored in appropriate containers. Samples transported for laboratory analysis will be packaged with the chain of custody (COC) manifest will be prepared (see example in Appendix A). A copy of the COC will be maintained and the initial disposition will be noted on the data collection form. The laboratory will also return a copy of the signed and dated COC to the sender upon receipt and acceptance.

10.0 Quality Assurance

Generation of quality chemistry data is essential for supporting the 2009/2010 Heavy Metals Assessment Study Within the 6TREATY Tribes Historic Jurisdictional Lands. To avoid problems associated with data reliability, it is necessary to implement adequate quality assurance measures in the sampling program, during data collection and analysis. In this study, the quality

of data analyzed by portable XRF will be evaluated by conducting laboratory analysis of a minimum of 5% of the field-collected samples. Samples for XRF analysis will be dried to a constant weight at the University of Tulsa (TU) in Tulsa, Oklahoma. The dried samples will be sent to the Trace Element Research Laboratory, Texas A & M University, College Station, Texas. The samples will be sieved to <63 microns and analyzed with the XRF using EPA Method 6200 by certified tribal personnel. Tribal personnel in the will direct quality assurance and control during XRF analysis.

Split samples, discussed in section 6.1 above, will be collected by placing alternating spoonfuls of soil into different bags, or placing half of each scoop into each bag. A minimum of one split sample will be collected per day of sampling.

The samples selected for confirmatory chemical analysis will digested using EPA Method 3052 (Microwave assisted acid digestion of siliceous and organically based matrices) and analyzed by ICP-AES using EPA Method 6010B.

11.0 Examples of Forms for Sampling Event

Examples of forms that will be used for this sampling event are presented as addenda, including the data collection form and chain of custody form (Appendix B).

12.0 References

Dames & Moore, 1995, Final Remedial Investigation: Neck/Alba, Snap, Oronogo/Duenweg, Joplin, Thoms, Carl Junction, and Waco Designated Areas, Jasper County Site, Jasper County, Missouri.

Eisler, R. 2000. Handbook of chemical risk assessment Health hazards to humans, plants, and animals. Volume 1.

EPA. 1996 Standard Method 3052: Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices.

EPA. 1996 Standard Method 6010B: Inductively Coupled Plasma-Atomic Emissions Spectrometry

EPA. 1998 Standard Method 6200: Field Portable X-Ray Fluorescence Spectrometry for the Determination of the Elemental Concentrations in soil and Sediment. 31pp

Appendix A – Health and Safety Plan

**Heavy Metal Assessment Study Within the
6TREATY Tribes Historic Jurisdictional
Lands Health and Safety Plan**

November 4, 2009

Prepared by:

6TREATY Tribes of Oklahoma

Introduction

This Health and Safety Plan has been developed as part of the Heavy Metals Assessment Study Within the 6TREATY Tribes Historic Jurisdictional Lands soil sampling effort planned for December 2009/January 2010. The sampling effort will include collection of 70 soil samples in Ottawa and Delaware counties of Oklahoma. Additional details about the sampling effort are provided in the document in the main body of this document. A copy of this Health and Safety Plan should be kept with each sampling team during this sampling effort.

DIAL 911 IN ALL LOCATIONS IN CASE OF EMERGENCIES

Sampling Operations

Sampling operations: Sampling operations and plans will be discussed at a meeting prior to sampling. Each day prior to commencing work a meeting will be held by the team leader informing all members of the type and location of safety gear, as well as the anticipated activities for the day, during a pre-departure safety “tailgate” meeting.

Sampling Locations: Soil sampling will take place throughout the tribal historic jurisdictional areas. Sampling locations have been determined prior to sampling and locations have been loaded into GPS units.

Weather: Cold weather conditions are expected in the mornings with warmer weather expected in the afternoons. It is recommended that personnel dress in layers and bring sunscreen to avoid sun exposure. Inclement weather severe enough to disrupt sampling operations is not anticipated. However, National Weather Service broadcasts will be monitored. Sampling activities may be modified based on weather reports or weather conditions experienced while on-site. In all cases, sampling will occur only under conditions deemed safe by Meredith Garvin and/or team leader.

Hazards: There are many hazards associated with working outdoors, including slips, trips, and falls; sun exposure, poison ivy and cuts and scrapes from vegetation.

Safety Equipment

All vehicles will have a first aid kit and at least one cell phone to contact emergency personnel.

Safety Rules

- No sampling will occur before sunrise or after dark
- No sampling will occur without landowner permission
- No illegal drugs or alcohol are allowed on board the vessel; and

Communications

Teams will exchange cell phone numbers before embarking into the field. Teams will check in every four hours with Meredith Garvin. In case of inclement weather, teams will contact each other and proceed to the boat ramp.

Emergency Phone Numbers

Telephone numbers of local emergency service providers in the vicinity of sampling locations are listed below. For contact information of field personnel, see the Communications section of this plan.

DIAL 911 IN ALL LOCATIONS IN CASE OF EMERGENCIES

NEAREST HOSPITALS/ CLINICS

Miami, Oklahoma

Integris Baptists Regional Hospital
200 Second Avenue SW
Miami, OK 74354
Telephone Number: (918) 542-6611

Joplin, Missouri

St. John's Regional Medical Center
2727 McClelland Blvd.
Joplin, MO 64804
Telephone Number: (417) 781-2727

Appendix B – Tables

Table 1. Sampling Equipment Required to Support the Heavy Metals Assessment Study

Cleaning Supplies							
Liquinox		Water buckets (2)					
Squirt bottles		DI water					
Sampling Supplies							
Glass jars, 4 oz., Qty 15 - 20				Stainless steel spoons			
Water proof labels				Large ice chests w/ice			
Gloves							
Van Doren Sampler							
Stainless steel trowel							
Scrub brush							
Teflon lined trays, Qty 2							
Measurement Supplies							
<63 microns sieve							
One gallon ziplock bags							
Shipping and Storage Supplies							
Personal supplies							
Miscellaneous supplies							

Table 2. Volume, Container Material, Preservation Specifications, and Holding Times for samples collected for Heavy Metals Assessment Study.

Parameter Analyzed	Laboratory	Approximate Volume	Container Material	Preservation Method	Holding Time
Metals (by XRF)	Texas A & M				
Metals (by EPA Method 6010B)	Approved FWS lab-				
	TBD				

1 day; XRF = X-Ray fluorescence;

Table 3. Contamination of Potential Concern and Data Quality Objectives For the Heavy Metals Assessment Study (applicable to confirmatory chemistry by Method 6010B only.)

Contaminant	Target	Target Mean	Target	Target
Potential Concern	Detection Limit (as μL digestate)	Accuracy (Average % Recovery)	Precision (Relative Standard Deviation %)	Completeness
Metals (mg/kg)				
Lead	2.3	75-125	20	100%
Cadmium	28	75-125	20	100%
Chromium	1.2	75-125	20	100%

Appendix C – Sampling Forms

Data Collection Form

Sample site Name:

Sample Site Number:

Names of Sampling Personnel:

Sampling Date:

Sampling Time:

Latitude and Longitude:

(including instrumentation used and any problems encountered)

Weather conditions:

Precipitation

Wind Speed

Type of sampler Used:

Sample Depth:

Unusual events during sampling:

(i.e., sampler did not close completely, etc)

Description of sample:

(i.e. sand, clay)

Description of sample color: (i.e., black, brown, etc.)